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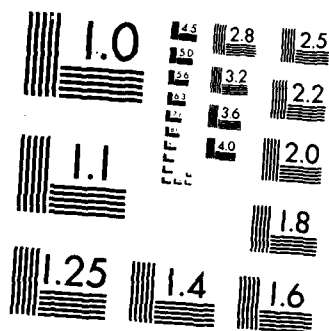Final Technical Report
September 1986

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A STUDY OF THE ENHANCED THERMIONIC EMISSION OF MOLYBDENUM, HAFNIUM AND ZIRCONIUM DUE TO DISPENSER CATHODE EXPOSURE

University of Utah

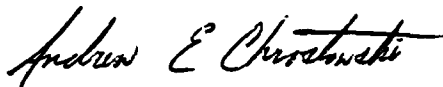James B. Hickey

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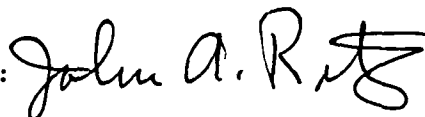
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Hafnium, zirconium and molybdenum were studied in a tube environment to determine their levels of thermionic emission following exposure to a 4:1:1 dispenser cathode operated at a brightness temperature of 1050°C. In order to obtain a curve of equilibrium emission density versus temperature, the temperature of the sample under study was varied above and below that of the source. Once equilibrium was reached at each temperature, the emission was recorded. Variations in surface temperature alter the Ba/BaO coverage, and hence the work function. The change in work function with coverage is much greater for low coverages and the measured emission therefore followed the typical S-shaped variation of metals placed in alkali and alkaline-earth vapor streams. From emission densities the effective work functions of the surfaces studied were claculated. Before exposure to the source cathode, calculated effective work functions were in good agreement and published values. Thermal emission densities of hafnium and zirconium, after equilibrium exposure at the same temperature as the source, were found to be on the order of only a few microamperes.

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Chapter I

INTRODUCTION

Modern ECM systems are increasingly specifying the use of high duty gridded TWT's. Operating a high power pulse tube at high duty necessitates the use of a shadow grid to reduce beam interception by the control grid. Otherwise, high grid currents would result, causing design problems for the grid modulator or control grid destruction by overheating.

To reduce focusing aberrations, the shadow grid must be placed on, or very close to, the cathode surface. Over time, the shadow grid becomes, to at least some degree, covered with barium and barium oxide evaporated from the dispenser cathode. Any degree of Ba/BaO coverage will cause a reduction of the shadow grid work function and, therefore, an increase in its thermal emission. This gives rise to the high grid current the shadow grid was designed to prevent. To prevent this from occurring, two strategies may be adopted: (1) select a grid material or coating which maintains a relatively high work function under conditions of Ba/BaO adsorption, or (2) choose a material or coating which will allow only a very small coverage at the elevated shadow grid temperature (approximately 1400°K).

The object of this study was to evaluate various grid materials for thermal emission during simulation of the actual shadow grid/cathode equilibrium. The materials selected were molybdenum, hafnium and molybdenum coated with a tungsten diffusion barrier over which zirconium was sputtered. Great care was taken to ensure that all materials were handled and processed as the actual grids were handled. Comparison of the results is on the bases of the measured

emission current densities and the effective work functions derived from those results. The validity of such comparisons is discussed.

Chapter II

THE TEST VEHICLE

2.1   Design

The test vehicle was chosen for simplicity of construction and consisted, essentially, of "sandwiching" a movable shutter between two standard electron gun envelopes. Only the shutter and receiver required special fabrication.

Two indirectly heated planar surfaces, one a barium source (a 4:1:1 tungsten matrix cathode) and the other the material to be tested for thermal emission (the "receiver"), were separated by a gravity-actuated shutter as depicted in Figure 2.1. When the shutter was opened, the receiver was exposed to the barium source; when closed, the shutter served as an anode. The emitting surfaces were 1/2" in diameter, sufficiently large to provide (under conditions of barium adsorption) an emission current great enough to be measured by an ordinary ammeter and considerably greater than any normal ohmic leakage. Emission measurements were made by rotating the test vehicle 180 degrees to allow the shutter to slide closed, and then recording the value of current indicated on a Keithly 179A multimeter.

2.2   Choice of Design

This design was selected to simulate the equilibrium situation which is present in an actual grid/cathode system, in order to obtain a comparison of emission suppression materials in as uncomplicated a manner as possible. Due to the overwhelming effects of control grid and shadow grid alignment, earlier experiments by other workers, which aimed at duplicating the actual shadow grid/cathode system, provided only contradictory results.
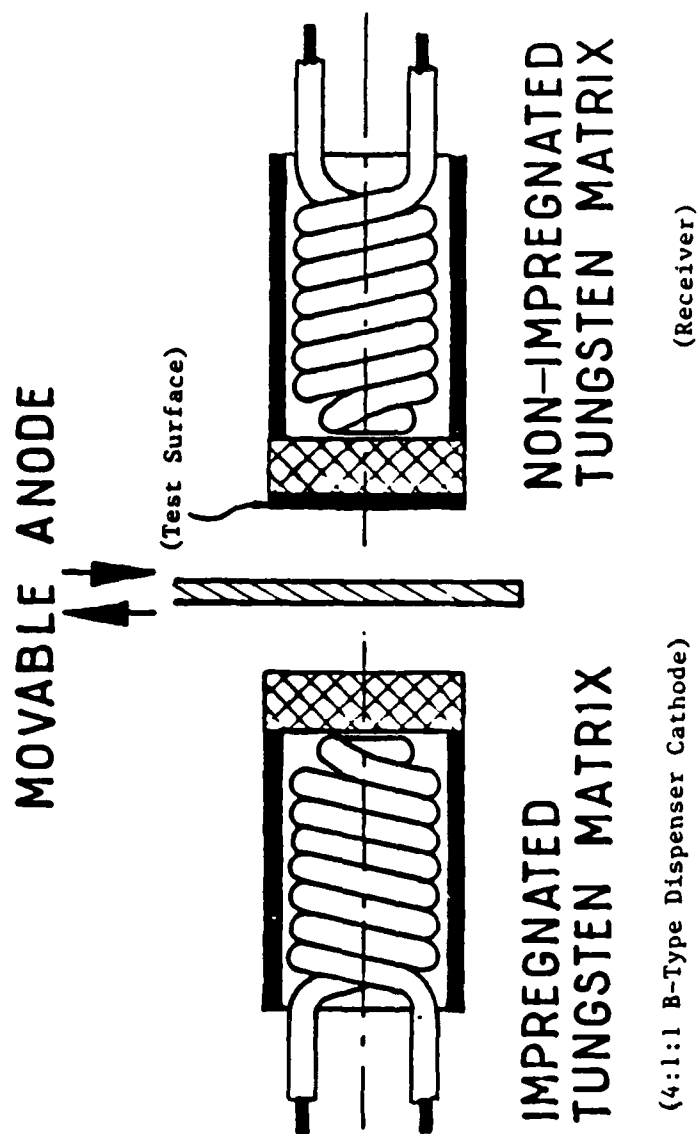
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Figure 2.1. Sketch of the test vehicle.

Chapter III

EXPERIMENTAL PROCEDURE

3.1 Outline

Surface temperatures of the receiver and source, operating in their electron gun assemblies, were determined by optical pyrometry while viewing through a small hole in a temporary anode. The filament currents, voltages and corresponding temperatures were recorded. From these values, a plot of temperature versus filament current was obtained for each surface. With the aid of this information, the barium source could be maintained at a known brightness temperature and the receiver temperature could be varied by a known amount above and below this value. The open shutter receiver current, monitored with the aid of a strip chart recorder, was observed until a steady state of emission current was obtained at any given receiver temperature. Then, by rotating the test vehicle 180 degrees, the shutter was closed and an emission measurement taken. From the value of emission current obtained, the effective work function of the receiver was calculated.

3.2 Determination of Equilibrium

To allow the surface to reach equilibrium, the current was monitored with the shutter open. However, opening the shutter increases the receiver/shutter separation and, therefore, the space charge effects. Given the low values of accelerating potential applied in order to reduce the power delivered to the shutter, it might be expected that in the case of large currents (milliamps as opposed to microamps) operating with the shutter open might cause the emission to be space charge current limited. If this were the case, the emission would

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be limited to one value of current density, given by Child's law ($J_{tl} > J_{sc}$), at any given applied potential and receiver/shutter separation, regardless of the changing condition (i.e., work function and/or temperature) of the surface under test. Fortunately, this circumstance was never observed. An equation which describes the actual situation has been obtained empirically by Longo[1], namely

$$J = J_{tl}J_{sc}/(J_{tl} + J_{sc}) \tag{1}$$

where

$$J_{tl} = AT^2e^{-\phi/kT} \tag{2}$$

and

$$J_{sc} = (4\varepsilon_0/9)(2\ eV^3/md^4)^{1/2} \tag{3}$$

A is the effective Richardson constant, ϕ the work function in eV, k Boltzmann's constant, T the surface temperature, ε_0 the permittivity of free space, e the charge of an electron, V the voltage applied between emitter and anode, m the mass of an electron and d the separation of emitter and anode. Using this equation, current density versus voltage for a surface of varying work function or, equivalently, varying degrees of barium coverage may be calculated. Figure 3.1 presents

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[1] R. T. Longo, "A Study of Thermionic Emitters in the Regime of Practical Operation." IEEE, 1980.

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Figure 3.1. Calculated current density, according
to Longo's equation, of a close-spaced
diode. (T = 1400°K)

the results of such a calculation for a receiver/shutter separation of 0.015 inch.

It is apparent from such plots that, even at values of applied field as low
as 5 to 10 volts, any changes in barium coverage should be detectable, and are.
The changing emission current, corresponding to the changing work function
prior to equilibrium, allows the varying surface conditions to be monitored under
what might commonly be considered conditions of space charge limitation.

Chapter IV

METHOD OF DATA ANALYSIS

To obtain the zero field current density, corrections must be made for space charge effects and for the effects of the applied accelerating field. Using Longo's equation

$$J = J_{t1}J_{sc}/J_{t1} + J_{sc} \tag{4}$$

for the observed current density, the temperature-limited current density

$$J_{t1} = AT^2e^{-\phi/kT} \tag{5}$$

can be calculated, since the space charge limited current density for planar geometry

$$J_{sc} = (4\epsilon_o/9)(2\ eV^3/md^4)^{1/2} \tag{6}$$

is known. If the temperature at which the emission measurement was taken is also known, an effective work function (ϕ) for the emission suppression material under test can be calculated and used as a basis of comparison. The usefulness of such comparisons will be discussed later.

Chapter V

RESULTS

5.1   Molybdenum Receiver

Prior to the initial exposure of the molybdenum to the barium source, the work function of the surface was measured to be near 4.7 eV. The published values for molybdenum range from 4.36 eV to 4.95 eV, with the majority between 4.5 eV and 4.6 eV. The close agreement to published values leads one to believe that using the filament current as the indicator of surface temperature does provide results which may be trusted. (Also, depending upon the choice of emissivity as discussed in the concluding section, the work function calculated may have been increased by a further few tenths of an eV. This would place the actual value nearer to 4.5 eV.)

After exposure to the barium source, the work function was measured to be about 2.46 eV for a receiver/source equilibrium temperature of approximately 1400°K (determined from a source brightness of 1050°C$_b$ and assumed emissivities of 0.46 for tungsten and 0.37 for molybdenum — values obtained from the CRC Handbook of Physics and Chemistry). The results of the equilibrium measurements are presented in Figures 5.1 and 5.2. A work function minimum, not shown in the plotted data, was found to occur about 1180°K. Figure 5.3, for the extensively studied tungsten/cesium and tungsten oxide/cesium systems, is reproduced from Dobretsov and Gomoyunova.[2]

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[2] L. N. Dobretsov and M. V. Gomoyunova, Emission Electronics, Jerusalem, 1971, p. 148.

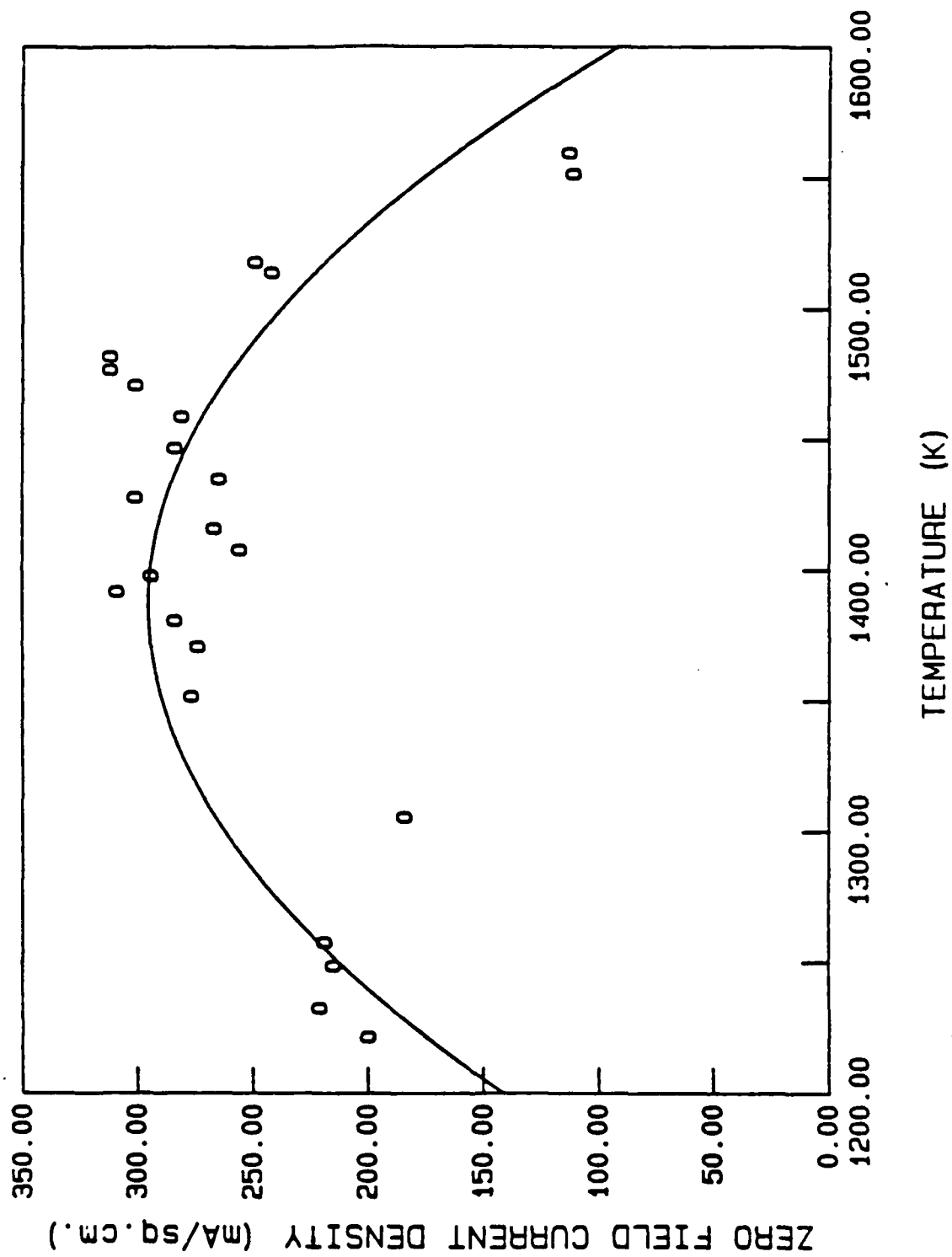Figure 5.1. The equilibrium emission of molybdenum following dispenser cathode exposure (source temperature approximately 1400°K).
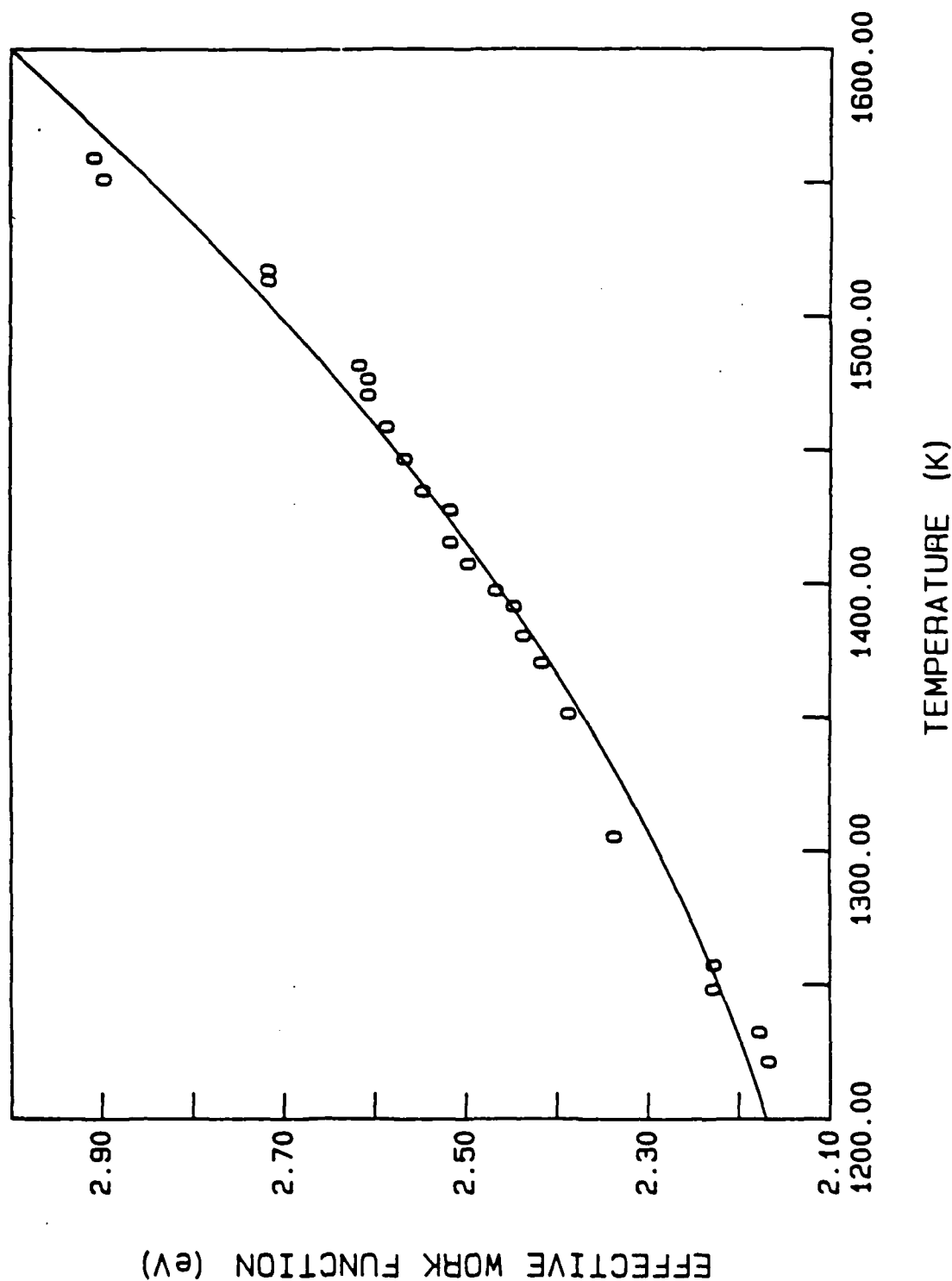
Figure 5.2. The effective work function of molybdenum following dispenser cathode exposure (source temperature approximately 1400°K).
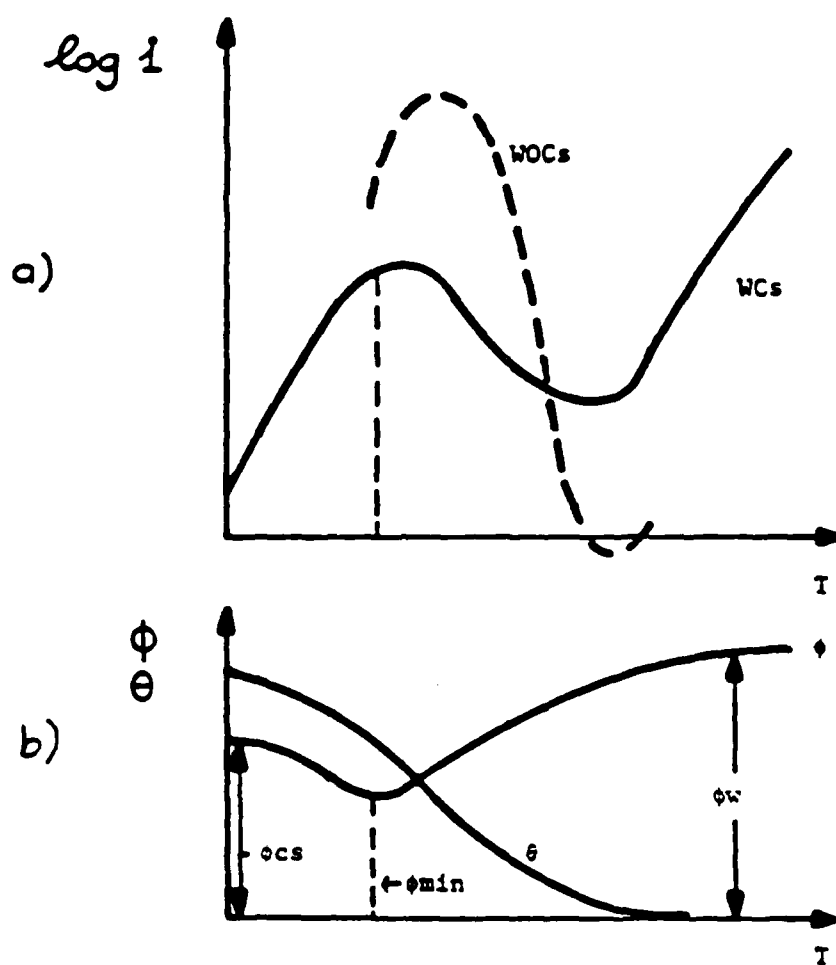
Figure 5.3. The S-shaped variation of thermionic emission
with variation in temperature and coverage of
tungsten and tungsten oxide in a cesium vapor.

Due to the temperature at which the minimum work function for the Ba-Mo system occurred and the general applicability of Figure 5.3 to other thermionic surfaces placed in gas/vapor streams, it is presumed that the curve of emission density should follow the local maximum of the S-shaped variation of Figure 5.3(a). A quadratic least-squares-fit to the data follows such a variation. The characteristic S-shape in Figure 5.3(a) is due to the non-linear change in work function, ϕ , with change in barium coverage, θ ; for low coverages, the change in work function with change in coverage is greatest and decreases as completion of the monolayer is approached.

The surface is free of adsorbed atoms at high temperatures. Its work function is approximately constant, and any increase or decrease in temperature gives rise to an increase or decrease in emission according to Richardson's equation. If the temperature is lowered sufficiently, an accumulation of adsorbed atoms begins; the increase in emission due to the decrease in work function is, however, still less than the decrease in emission due to the decrease of temperature, and the emission declines. At some point, the increase in emission due to the decrease in work function becomes greater than the decrease in emission due to the decrease in temperature; the emission reaches a minimum, then rises. If the temperature is further decreased, the coverage continues to increase but the rate of decrease in work function with decrease in temperature slows; at some point, the reduction in temperature begins to predominate and the emission will pass a maximum. After this maximum, a decrease in temperature produces only a decrease in emission since very little decrease in work function occurs after this point.

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5.2   Hafnium Receiver

The work function of the hafnium surface, before initial exposure to the barium source, was measured to be 4.04 eV at about 1431°K. The variation in emission density with temperature of the hafnium surface after equilibrium exposure to the barium source is displayed in Figures 5.4 and 5.5. (The meaning of the arrows in Figures 5.4 and 5.5 is discussed in Chapter IV.) As can be seen in Figure 5.5, which is a plot of effective work function versus receiver temperature, the observed effective work function above approximately 1425°K is that of the "bare" hafnium. At about 1400°K (the assumed equilibrium temperature of an actual shadow grid/M-type cathode system calculated from a source brightness temperature of 1050°C and using a value of 0.44 for the emissivity of hafnium) the work function is hardly lowered or, equivalently, the emission current density is hardly raised. The value of the effective work function at this point, as shown in Figure 5.5, is lowered by only 0.1 eV from its asymptotic maximum of around 4.1 eV. These observations indicate that the superior emission suppression characteristics of hafnium, as compared to molybdenum, are due to an incapability of the hafnium surface to adsorb barium/barium oxide at the normal operating temperature of the M-type cathode/grid system. Such a slight change in work function can only be due to a very light coverage at these high temperatures. Applying a phenomenological theory of Gyftopoulos and Levine[3], the expected work function of hafnium would be in the vicinity of 3.0 eV were the coverage about the same as for barium on molybdenum. While not so significant in terms

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[3] E. P. Gyftopoulos and J. D. Levine, "Work Function Variation of Metals Coated by Metallic Films," Journal of Applied Physics, January, 1962, 33:67-75.

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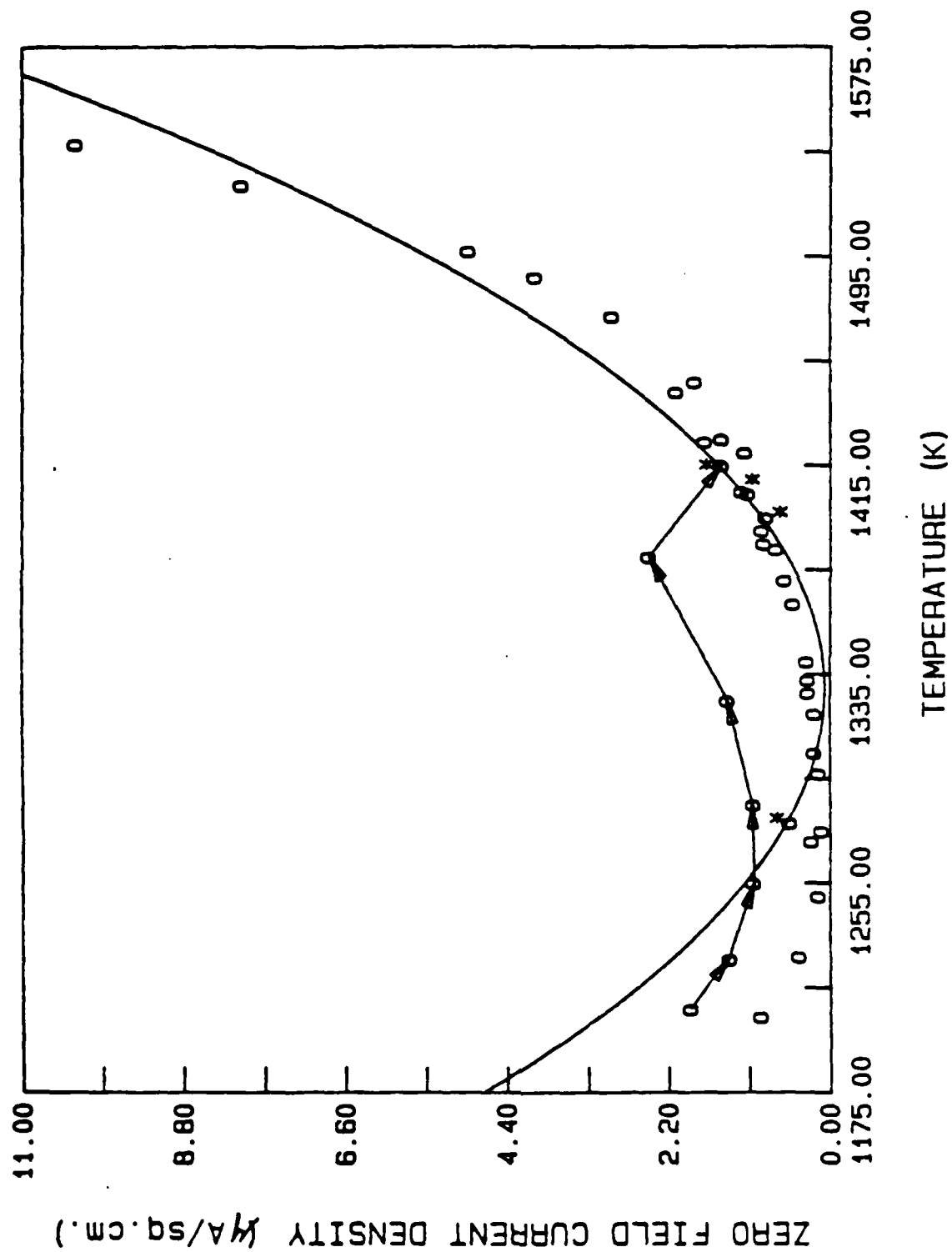Figure 5.4. The equilibrium emission of hafnium following dispenser cathode exposure (source temperature approximately 1400°K).

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EFFECTIVE WORK FUNCTION (eV)

TEMPERATURE (K)

1575.00 1475.00 1375.00 1275.00 1175.00
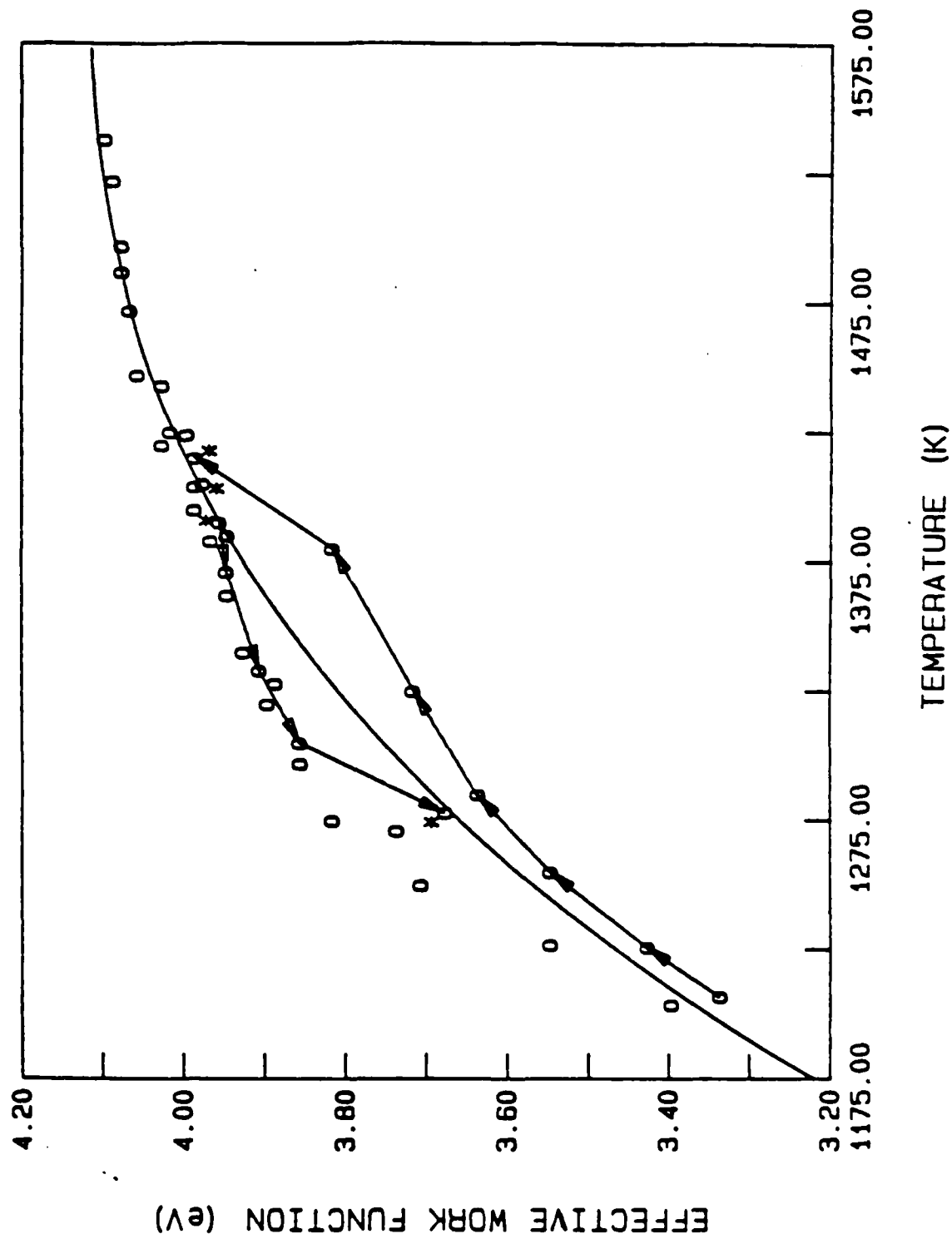
4.20 4.00 3.80 3.60 3.40 3.20
1175.00

Figure 5.5. The effective work function of hafnium following dispenser cathode exposure (source temperature approximately 1400°K).

of reduced emission as the measured value of 3.99 eV, even this value would be an improvement over the 2.46 eV measured for molybdenum. This is interesting in view of the fact that molybdenum has an advantage of about 0.7 eV in terms of its higher work function prior to adsorption of the barium/barium oxide. It is easy to see why hafnium has been reported to be such a good suppressor of emission.

5.3 Zirconium Receiver

The effective work function of the zirconium surface, prior to the initial exposure to the barium source, was measured to be about 4.03 eV. The variation in emission density and effective work function with temperature, after equilibrium exposure to the source, is displayed in Figures 5.6 and 5.7. The emission density above approximately $1450°K$ (calculated from brightness temperatures using a value of 0.40 for emissivity) corresponds to the "bare" surface.

In comparison with the results for hafnium, it can be seen that in the region of interest (i.e., surface and source at approximately the same temperature as in an actual cathode/shadow grid system) there is very little difference in emission density. Any observed difference in effective work function at the assumed equilibrium temperature are probably not within the resolution of the measurement method. A difference between the two does occur below about $1375°K$. Below this point, the thermal emission of zirconium appears to increase more quickly than that of hafnium. This may be due to an increased barium coverage on zirconium, or to a greater change in work function at the same coverage, or both. The almost immediate change in effective work function of zirconium suggests lesser adsorption and desorption energies for zirconium than hafnium.

Figure 5.6. The equilibrium emission of zirconium following dispenser cathode exposure (source temperature approximately 1400°K).

ZERO FIELD CURRENT DENSITY (μA/sq. cm.)
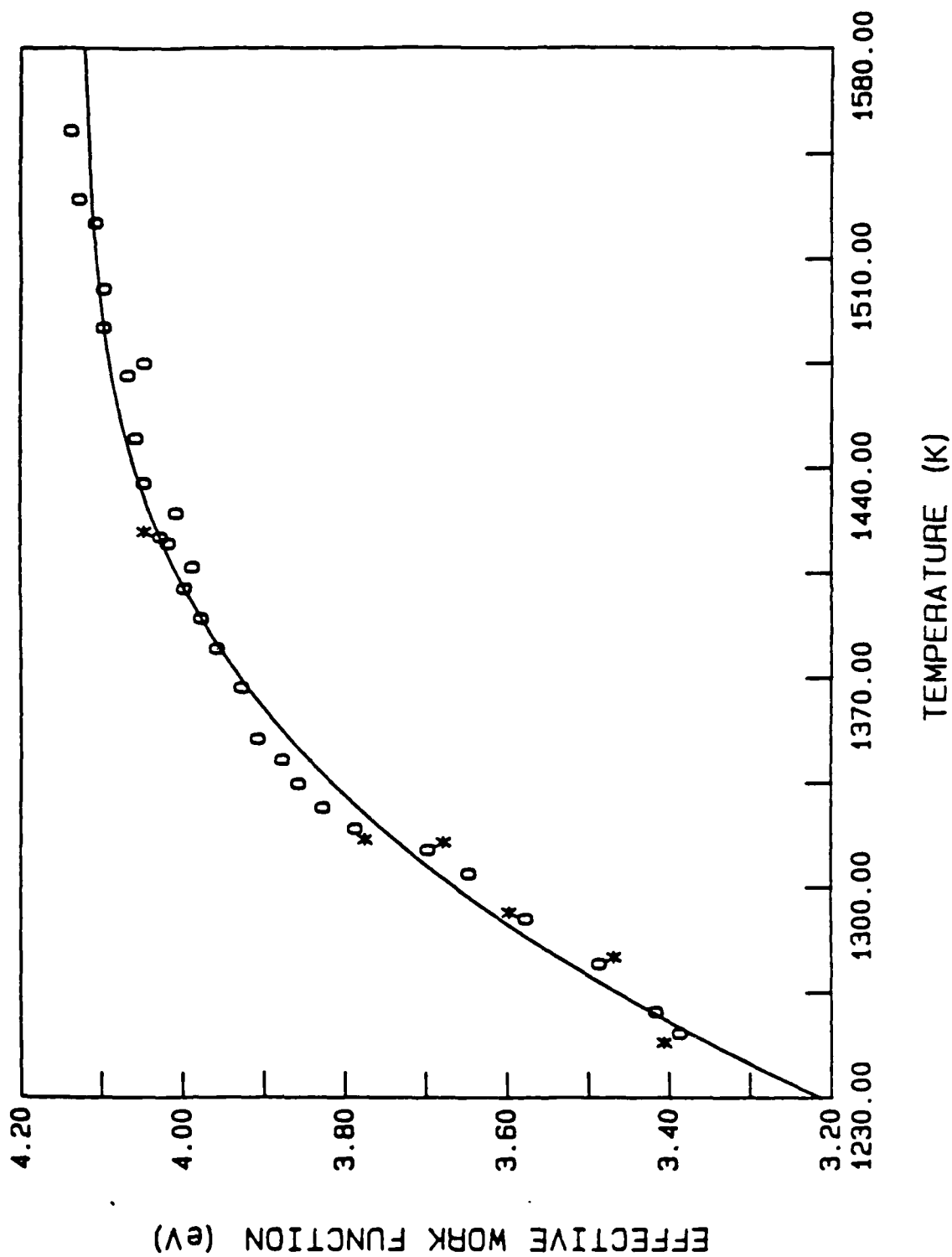
TEMPERATURE (K)

Figure 5.7. The effective work function of zirconium following dispenser cathode exposure (source temperature approximately 1400°K).

Very little, if any, difference in the emission of zirconium over time (at least 10 hours of exposure) was observed for the asterisked points in Figures 5.6 and 5.7.

Chapter VI

DISCUSSION OF RESULTS

6.1   High Current Density Measurement Errors

As regards measurement error in the case where space charge effects
are significant (i.e., the exposure of molybdenum to barium) the major source
was the slight play of the shutter necessary to ensure that it would slide when
heated.   Due to normal space charge effects, even a slight increase in
shutter/receiver separation will produce a large decrease in the measured current
density.   To control the position of the shutter, and thus the space charge when
taking measurements, the test vehicle was tilted so that the sliding anode was
resting on its lower support track.   In this position, the shutter was closest to
the receiver.

6.2   Attainment of Equilibrium

Unless great care and patience are applied to measurements, the data
points obtained may lie above or below the true curve (as shown, for example,
in Figures 5.4 and 5.5).   Whether a given measurement will lie above or below
depends upon the direction of temperature change one chooses (indicated by
the arrows of Figures 5.4 and 5.5) when measuring the emission.   The difference
between the "upward" and "downward" curves is probably due to a lag imposed
by the adsorption and desorption energies, adsorption occurring as the temperature
is lowered and desorption as it is raised.

For instance, the rate at which atoms are desorbed is dependent on the degree of coverage as well as the energy of desorption[4]

$$v_d = -c(kT/h)e^{-E_d/kT} \qquad (7)$$

where c is the concentration of atoms on the surface, k Boltzmann's constant, h Plank's constant, T the temperature of the surface and E_d the desorption energy. At equilibrium, the rate at which atoms are desorbed will equal the rate at which atoms impinge upon the surface and are adsorbed. Since the rate at which atoms impinge upon the surface is fixed by the temperature of the source, the less the desorption energy the longer will be the time taken to reach equilibrium for a given surface temperature.

The emission was monitored with the aid of a strip chart recorder, and periodic measurements by the multimeter were also noted. If there was no observed change in emission for about an hour, the emission was recorded. At the end of the series of readings, the experiment was left to run overnight and the emission was recorded the following morning. An asterisk indicates the results of the overnight measurements which amounted to at least ten hours of exposure to the barium/barium oxide source. The actual curve must lie very near to the points with the asterisk. The quadratic least-squares-fit to the zero-field current density is based upon these points.

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[4] This expression was derived on the assumption of an immobile surface layer. However, since the energy dependence does not change for desorption rates otherwise derived, this distinction is not relevant to what follows.

6.3   Uncertainty of Emissivity

The most probable source of error in these experiments was the lack of precise knowledge of emissivity for the thermionic surface being tested; emissivities and their temperature coefficients are, in general, not tabulated. (These values are required to obtain true temperatures from brightness measurements.) In instances where these have been determined, over variations in temperature of a few hundred degrees, the emissivity is not greatly altered. Some available values are presented in Table 6.1.

Table 6.1. Variations in spectral emissivity
at 0.65 microns.

Rough Graphite (1100 - 2000 K)
$$\varepsilon_{0.65} = (0.979 \pm .007) - (5.74 \pm 0.41) \times 10^{-5} T$$

Polished Graphite (1285 - 2035 K)
$$\varepsilon_{0.65} = (0.745 \pm 0.012) + (1.88 \pm 0.72) \times 10^{-5} T$$

Polished Carbon (1285 - 2035 K)
$$\varepsilon_{0.65} = (0.789 \pm 0.005) - (1.4 \pm 3.2) \times 10^{-7} T$$

Silicon (100 - 1688 K) etched and sandblasted
$$\varepsilon_{0.65} = 0.923 \pm 0.014 - (2.75 \pm .1) \times 10^{-4} T$$

Titanium (950 - 1380 °C)
$$\varepsilon_{0.65} = 0.522 - 3.15 \times 10^{-5} T$$

Polished Tungsten (1600 - 2800 K)
$$\varepsilon_{0.65} = 0.387 \pm .001 - (0.74 \pm .03) \times 10^{-5} T$$

The close agreement between the published work functions for molybdenum, hafnium and zirconium and those determined by current density measurements in these experiments indicates that the emissivities chosen to construct true temperature scales for the plots must be close to the actual values. Even so, since only relatively large differences in work function or, equivalently, emission density between materials are of interest, precise knowledge of emissivity is not required.

For example, the only available value of emissivity for hafnium close to the temperature of interest (approximately 1400°K) was found as 0.445 ± 0.008 at 1727°C. A value of 0.44 was used to construct a plot of filament current versus surface "true" temperature from the original brightness temperatures. If one makes the reasonable assumption that the actual emissivities of the receiver and source must lie between 0.2 and 0.8, Figure 6.1 shows the possible effects this uncertainty in emissivity might have on the location of the equilibrium temperature and, hence, the equilibrium emission density of hafnium.

Since the cathode was held at 1050°C$_b$ and its emissivity is assumed to lie between 0.2 and 0.8, its real temperature would have to have been in the range between 1342°K and 1464°K. All possible values for the equilibrium temperature must then lie between 1342°K on the 0.2 emissivity temperature scale (the lowest possible temperature of the receiver obtained from brightness temperature, assuming its emissivity must be in the range 0.2 to 0.8) and 1464°K on the 0.8 temperature scale (with the same assumption, the highest possible temperature of the receiver). All emission measurements to the right of the vertical arrow, regardless of temperature scale, do not differ from those of the bare hafnium.
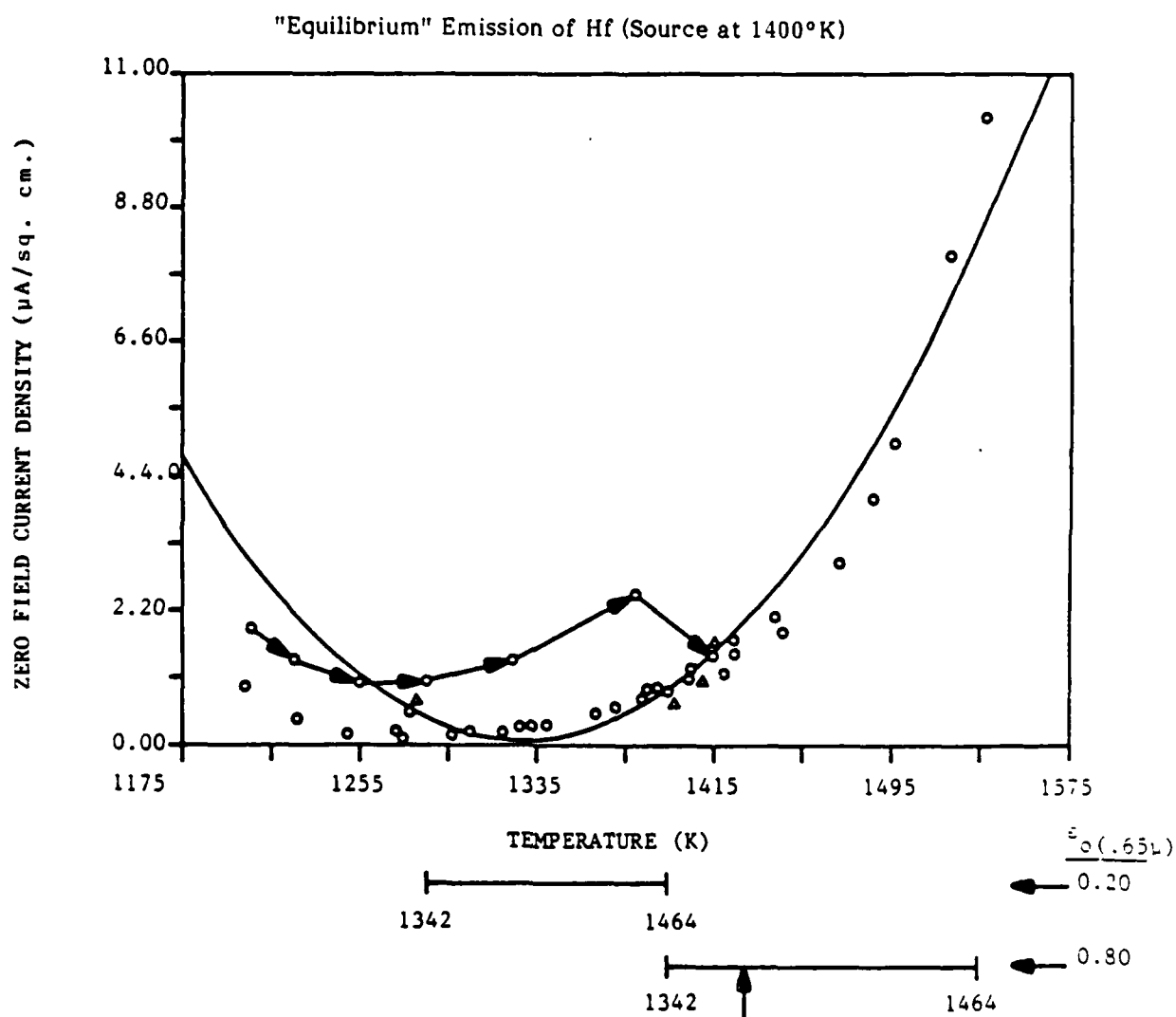
"Equilibrium" Emission of Hf (Source at 1400°K)

Figure 6.1. Effect of possible errors in the choice of
emissivity on the determination of the
cathode/receiver equilibrium temperature.

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This is the lowest emission that can be obtained from this surface at these temperatures. From the arrow and down to the lowest assumed possible temperature (1342°K on the 0.2 temperature scale) only a reduction in emission, as compared to that measured at the equilibrium temperature (approximately 1400°K), is obtained. Therefore, large differences between assumed and actual emissivities make little difference as regards the uncertainty in the location of the cathode/receiver equilibrium temperature and, hence, the equilibrium emission at that temperature. The emission remains quite low over the entire range of possible equilibrium values.

6.4   Apparent Temperature Variation of the Work Function

Maintaining the emissivity (used to calculate true temperatures from brightness temperatures) at a constant value will give rise to an apparent change in the work function of a constant work function surface as the temperature is varied. The direction of this apparent change will depend upon the temperature dependence of the true emissivity. Four possible situations may be distinguished and are displayed in Figures 6.2 through 6.5.

For the hafnium surface studied, when the emission was measured at various temperatures (prior to the initial barium source exposure) and the effective work functions were calculated from this data, the work function displayed a decrease in value with increase in temperature. Table 6.2 lists the results of a typical series of measurements for hafnium and zirconium. As can be seen from these results, for hafnium there was an observed decrease in effective work function of about 4.5E − 4 eV/degree with increase in surface temperature. For this decrease to occur, assuming that the work function actually remains constant

Figure 6.2 ε₀ is chosen too high and ε increases with an increase in temperature. This causes an apparent increase in the work function with an increase in temperature and the work function will appear lower than the actual value.

BRIGHTNESS TEMPERATURE

ε actual

ε used

ΔT1   ΔT2

TRUE TEMPERATURE

Figure 6.3   ε₀ is chosen too low and ε
              decreases with an increase
              in temperature. This causes
              an apparent decrease in work
              function with an increase in
              temperature and the work func-
              tion will appear higher than
              the actual value.

Figure 6.4 ε₀ is chosen too low and ε
increases with an increase
in temperature. This causes
an apparent increase in work
function with an increase in
temperature and the work func-
tion will appear higher than
the actual value.

BRIGHTNESS TEMPERATURE
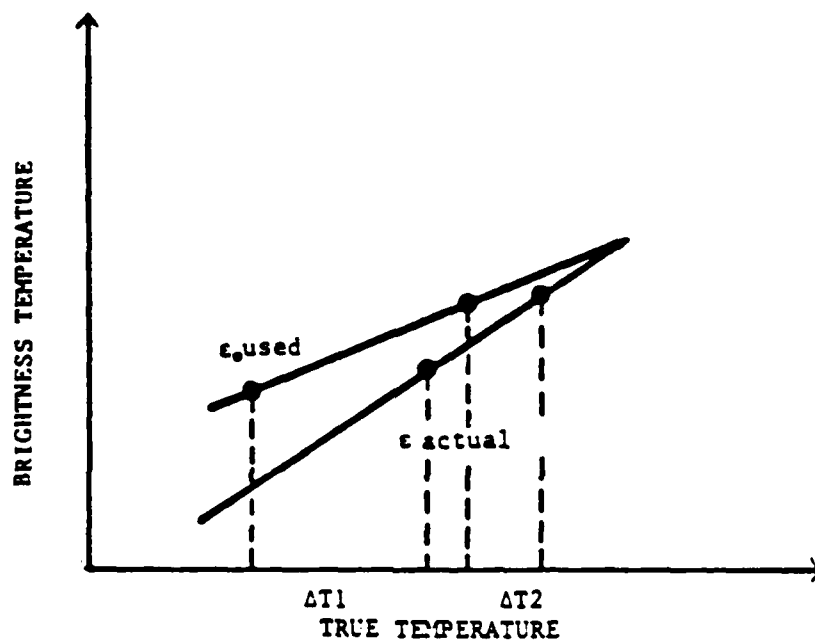
ε, used

ε actual

ΔT1   ΔT2

TRUE TEMPERATURE

Figure 6.5   εo is chosen too high and ε
decreases with an increase in
temperature. This causes an
apparent decrease in work func-
tion with an increase in tempera-
ture and the work function will
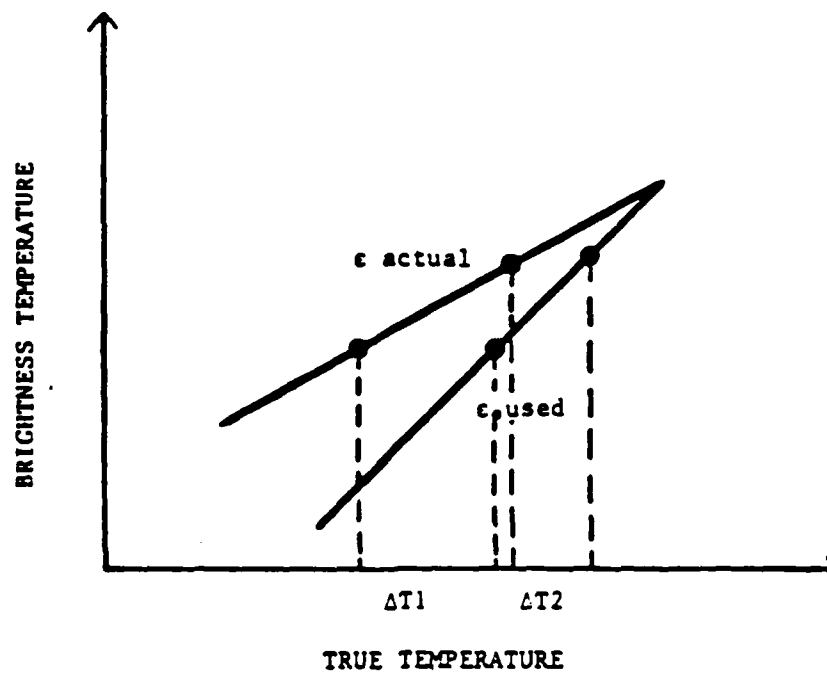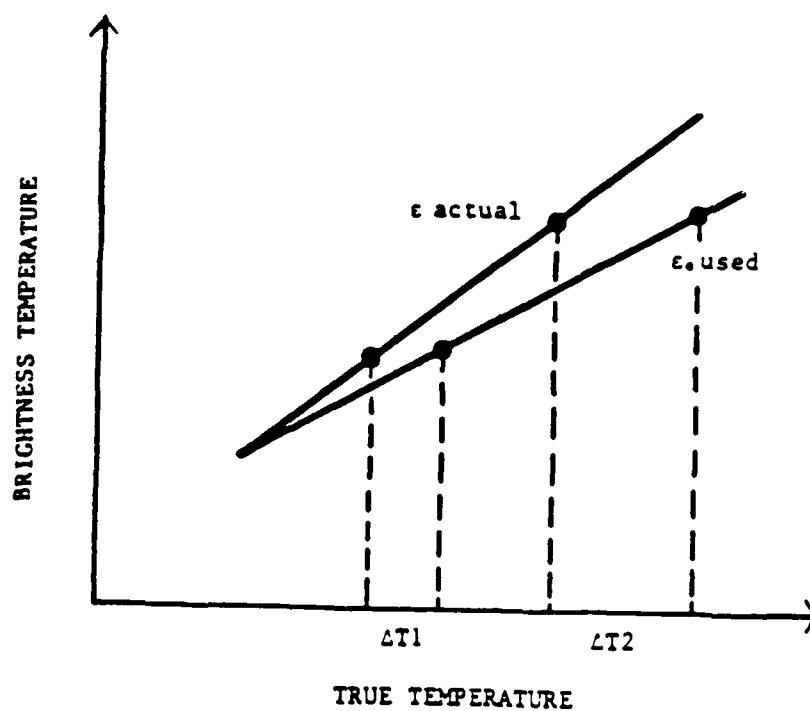appear lower than the actual
value.

Table 6.2

a: Typical Values of Effective Work Function
Measured at Various Temperatures for Hafnium
Prior to Initial Exposure To The Ba/BaO Source

Temperature (K)	Effective Work Function (eV)
1431	4.04
1452	4.01
1478	4.02
1500	4.00
1522	3.99
1545	3.99
1565	3.98
1586	3.97

b: Typical Values of Effective Work Function
Measured at Various Temperatures for Zirconium
Prior to Initial Exposure To The Ba/BaO Source

Temperature (K)	Effective Work Function (eV)
1356	4.02
1371	4.02
1401	4.03
1420	4.03
1442	4.04
1466	4.04
1487	4.05
1511	4.05
1540	4.07
1565	4.08

at 4.04 eV, the emissivity would be required to decrease at about 6.5E - 4/degree. This value is larger than any listed in Table 6.1. Assuming that the observed decrease in work function is due, at least in part, to a decrease in emissivity with increase in temperature, this would correspond to Figure 6.3. (Figure 6.5 also describes an apparent decrease in work function with an increase in temperature. However, since the most recent value for the work function of hafnium is given as 3.9 eV, it is assumed that Figure 6.3 corresponds. This value, lower than that measured in these experiments, is accepted on the bases of the validity of the experimental technique and best agreement with theoretical values of the true work function.[5])

Referring to Figure 6.3, any apparent decrease in work function with increase in temperature, due to such a temperature variation of emissivity, may be explained as follows. The emission is determined by the actual surface temperature. A decrease in emissivity corresponds to an increase in the true temperature for a given observed temperature and, if the selected emissivity ε_o (considered to remain constant with temperature) is chosen low, the temperature used to calculate an effective work function from the measured emission will exceed the actual value (by the amount $\Delta T1$ in Figure 6.3). The calculated effective work function will therefore appear greater than the actual value. As the temperature increases, the true emissivity, ε , decreases toward the chosen value, and the difference in temperature between that used to calculate the effective work

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[5] Chemical Rubber Company Handbook of Chemistry and Physics, 61st Edition, p. E-83.

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function and the actual surface temperature diminishes (i.e., $\Delta T2 < \Delta T1$); the work function appears to decrease in the direction of the actual value as the temperature increases.

This same phenomenon was observed in the case of the molybdenum and zirconium surfaces. However, the effective work function appeared to increase with temperature in both these cases, as opposed to the decrease in effective work function observed for the hafnium sample. For zirconium, the increase in calculated effective work function with increase in temperature may possibly be explained, at least in part, by the circumstances illustrated in Figure 6.2.

6.5   True Temperature Variation of the Work Function

A real variation of work function with temperature does exist, but the direction of change is unclear. The work function of a surface is determined by three quantities,

$$\phi = (W_a - m_s)/e \qquad (8)$$

where W_a is the electron affinity, m_s the Fermi level and e the normal charge of the electron. For metals, as well as other good conductors, the Fermi level always decreases with an increase in temperature.[6] By itself, this effect would give rise to an increase in work function of about $1E-4eV/degree$.[7] The electron

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[6] Wayne B. Nottingham, "Thermionic Emission," MIT Technical Report 321, December 10, 1956, p. 17.

[7] A. H. W. Beck, Thermionic Values, Cambridge, 1953, p. 10.

affinity is determined by the crystal structure of the surface and by the average dipole moment of any adsorbed atoms. For clean metallic surfaces, it is believed that W_a decreases with temperature increase[8] but the extent of this decrease is not known. Therefore, depending upon the relative change of the electron affinity and the Fermi level, the true work function may increase or decrease with a change in temperature but the amount, although small, cannot be predicted.

6.6   Effective Work Functions

The usual method of deriving work functions, from thermionic emission data, is to calculate them from the Richardson-Dushman equation, $J = A_o T^2 \exp(-\phi/kT)$, using the universal value of 120 amperes/$(cm^2 - K^2)$ for A_o, Richardson's constant. Work functions obtained in this manner implicitly contain not only the effect of electrons reflected at the metal surface but, more importantly, the effects of surface patchiness.

Two main assumptions are made in the derivation of the Richardson-Dushman equation: (1) the emitting surface is uniform, and (2) only a very weak field is necessary to produce saturation. Corrections for the latter can be easily made by taking into account the Schottky effect. As far as the former is concerned, many emitting surfaces are far from uniform. In fact, they consist of an unknown number of patches of unknown individual area and work function.

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[8]W. B. Nottingham, op. cit., p. 17.

If the applied field is much stronger than the patch field (i.e. the field outside the emitter due to the difference in work function of neighboring patches), the apparent work function ϕ^{**} for the composite surface is given by

$$\phi^{**} = \Sigma w_i \phi^*_i \tag{9}$$

where ϕ^*_i is the apparent work function of the ith patch, and w_i the fraction of the total zero-field current contributed by that patch. ϕ^{**} is the quantity usually derived from Richardson plots. Analysis shows that ϕ^{**} is heavily biased toward the lowest work functions of the surface.[9] Therefore, depending upon surface patchiness, measured effective work functions would be expected to differ from the preferred values found in many references measured for single crystals.

Furthermore, the Richardson-Dushman equation, in its usual form, does not explicitly include the temperature dependence of the work function. The form of this equation which includes these effects is given as

$$J = A_o \bar{D} T^2 \exp(-e\alpha/k) \exp((-\phi(T_o) - e\alpha T_o)/kT) \tag{10}$$

A_o is the universal Richardson constant (120 amperes/(cm^2 - K^2)), $\bar{D}$ is the average coefficient of transmission, α is the temperature coefficient of the work function. $A_o \bar{D} \exp(-e\alpha/k)$ is the apparent Richardson constant published in tables of thermionic "constants" and T_o is the point about which $\phi(T)$ may be expanded to obtain the Taylor series

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[9]J. C. Riviere, <u>Solid State Surface Physics</u>, Min. Green, ed., New York, 1969, p. 185.
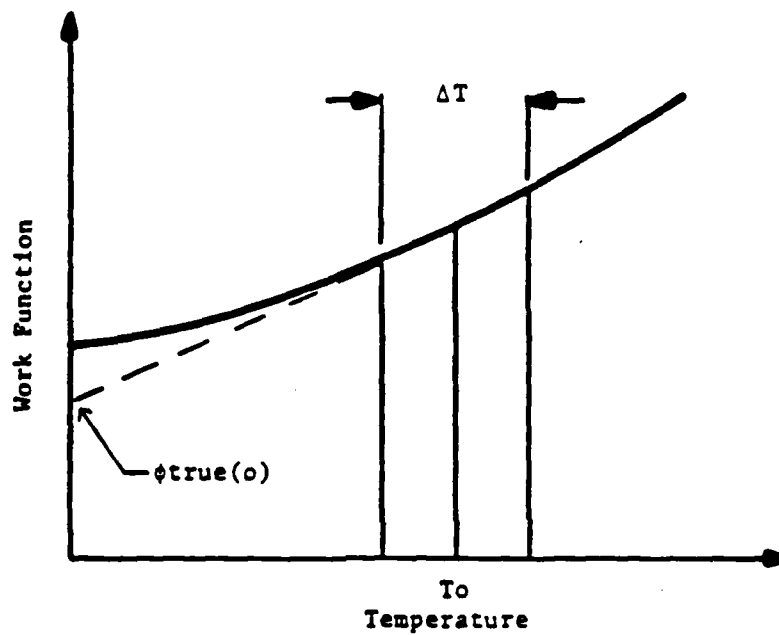
Figure 6.6   Diagram for the Taylor Series
Expansion of the work function
around To.

$$\phi(T) = \phi(T_O) + (d(\phi)/dT)(T - T_O)$$

$$= \phi(T_O) + \alpha(T - T_O) \tag{11}$$

which is used in this approximation.[10]

In order to make explicit the functional dependence of the effective work function (neglecting for the moment effects of patchiness), the Richardson and temperature dependent equations of emission are equated. Then, substituting $\phi_{true}(0) = \phi(T_O) - e\alpha T_O$ into the temperature dependent equation, it follows that

$$A_O T^2 exp\,(-\phi_{meas.}(T)/kT) = A_O \bar{D} T^2 exp(-e\alpha/k)exp(-\phi_{true}(0)/kT) \tag{12}$$

or

$$exp(-\phi_{meas.}(T)/kT) = \bar{D}exp(-\phi_{true}(0)/kT - e\alpha/k). \tag{13}$$

Therefore,

$$\phi_{meas.}(T) = \phi_{true}(0) + e\alpha T - kT(ln\bar{D}). \tag{14}$$

But,

$$\phi_{true}(0) = \phi_{true}(T) - e\alpha T \tag{15}$$

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[10]For a more detailed discussion of the problem, see Dobretsov and Gomoyunova, op. cit., pp. 92-97.

so

$$\phi_{meas.}(T) = \phi_{true}(T) - kT(\ln\bar{D}). \tag{16}$$

The explicit temperature dependence of $\bar{D}$ is unknown but its effect on the calculation of the work function is small. For example, the value of $\bar{D}$ for metals is very close to 1 but assuming even an unrealistically low value of 0.5 at a temperature of 1415°K, the difference between the true and effective work functions amounts to an increase of only 0.08 eV.

6.7   Comment on Comparison of Emission Data

For the above reasons, there can be no absolute validity in the comparison of computed effective work functions between these experimental results and those determined by similar emission methods — unless one can be assured that the samples were identical and under the same vacuum conditions. For years, the preferred value for a well-outgassed sample of hafnium was considered to be 3.53 eV.[11] The real value of such derived work function values, as well as the "emission constants" (i.e., work functions and Richardson constants)[12] obtained by the usual methods is in the determination of qualitative trends and/or in the relative comparison of surfaces under the same experimental conditions.

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[11]See, for example, the Chemical Rubber Company Handbook of Chemistry and Physics, 55th edition.

[12]J. C. Riviere, op. cit., p. 182.

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Chapter VII

CONCLUSIONS

The experiments reported here indicate that both hafnium and zirconium are suitable candidates for the suppression of thermal emission from grids. The low values of thermal emission measured for hafnium and zirconium indicate that only a very slight coverage of barium/barium oxide will be present on actual shadow grids fabricated from these materials, at or near to the usual operating temperature of dispenser cathodes (1000-1100°C$_b$). The maintenance of the relatively high work functions of these materials, due to the lack of adsorbed barium/barium oxide at cathode temperature, allows for thermal emission current densities on the order of only a few microamperes.

Therefore, in terms of emission suppression capabilities at least during relatively short total exposures on the order of hundreds rather than thousands of hours, very little distinction can be made between the two. One small difference appears to be a more rapid increase in the thermionic emission of zirconium with decrease in temperature (as the source temperature is held constant) below approximately 1370°K.

Finally, it must be emphasized that possible increases in emission with the applied field, due to neutralization of patch fields, have been ignored. The reason for this is that making such measurements did not prove to be possible while utilizing the present test vehicle design. However, any increase in emission of the zirconium and hafnium surfaces with an applied field is believed to be small due to the low surface coverages present at the elevated shadow grid

temperature. For small patches with work functions not differing greatly from that of the "clean" surface (corresponding to very low coverage), the effect is minimized.[13]

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[13]J. A. Becker, "Thermionic Electron Emission and Adsorption," _Reviews of Modern Physics_, 7:2 (April, 1935), 95-128.

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